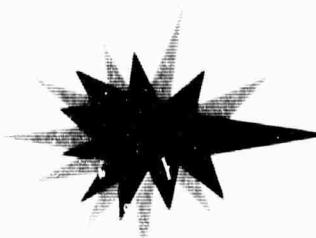


25 years of research



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March 29, 1962

AD6126781

Director of Aerospace Sciences
AF Office of Scientific Research
Washington 25, D. C.

Attention: SRHP

Gentlemen:

This letter constitutes the third quarterly progress report on the contract described below.

"Analytical Investigation of Combustion Instability
in Solid Propellant Rockets"

ARPA Order Number 24-61

Project Code Number 9100

Date of Contract: June 23, 1961

Contract Expiration Date: July 31, 1962

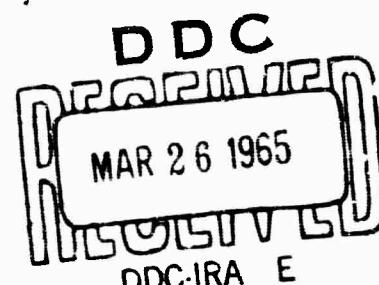
Amount of Contract: \$73,056

Contract Number: AF 49(638)-1094

Contractor: Armour Research Foundation
of Illinois Institute of Technology

Project Scientist: Dr. T. Paul Torda
CALUMET 5-9600, Ext. 2201

ARF Project No. D244



During March, W. J. Christian, F. Schuyler, and T. P. Torda of Armour Research Foundation attended the Second Meeting of the Technical Panel on Solid Propellant Combustion Instability. At that meeting, a review of the program was given. A copy of that review is appended to this letter and serves as a summary of the program up to March 1, 1962.

The month of March has been devoted to two general areas: 1) development of the finite-difference solution of the conservation equations for steady erosive burning with two-dimensional laminar flow and simplified

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reaction kinetics; and 2) study of the literature on the kinetics of gas phase reactions which are applicable to the solid propellant combustion. These investigations are proceeding at a satisfactory pace, such that we anticipate completion of the first fluid dynamic model, and evolution of a plausible kinetic scheme for at least one propellant system by the end of the present contract period.

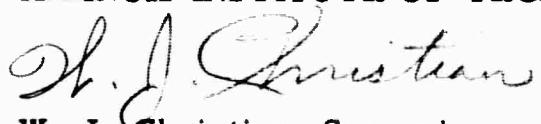
This avenue of investigation represents a departure from our previously stated goal (Quarterly Report No. 2) of first investigating a one-dimensional flow model representing burning without erosion. We had hoped to be able to include a fairly realistic representation of the chemistry in this model, thus it was our intention to simplify the fluid dynamics as much as possible in order to look closely at the chemistry involved. It has since become evident that development of a detailed chemical kinetic scheme cannot be completed in time for inclusion in the fluid dynamic model; hence, a simple kinetic scheme is being used. Thus, it is feasible to consider the more complicated two-dimensional flow model for the initial attempt at solution.

Solutions of the equations representing the fluid dynamic model will be generated using ARF's Univac 1105 computer. From a number of such solutions using various values of input parameters, the general behavior of the model and the effect of important variables can be investigated. Also, comparison of predicted burning rates with experimental data may be made. Because the numerical solutions will provide complete temperature, velocity and concentration profiles in the gas phase near the burning surface, the important features of the burning process will be evident. In particular, the effects of chemical reaction, parallel gas velocity, and mass diffusion in the induction zone will be found.

As indicated in the attached project review, we expect in the future to extend this treatment to include more realistic chemical kinetics as well as time variable phenomena.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY


W. J. Christian, Supervisor
Aerothermochemistry



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ANALYTICAL INVESTIGATION OF THE BURNING MECHANISM OF SOLID ROCKET PROPELLANTS

T. P. Torda and W. J. Christian
Armour Research Foundation of
Illinois Institute of Technology

Presented at the Second Meeting of Technical Panel on
Solid Propellant Combustion Instability, March 9, 1962
Contract No. AF49(638)-1094

The ultimate goal of this investigation is the evolution of a time-dependent theory for the erosive burning of solid rocket propellants. The approach being taken involves the use of a fluid dynamic model for the combustion zone. There is no doubt that the equations describing this fluid dynamic model in complete detail will pose an extremely difficult problem; however, there is uncertainty at present concerning the form which a proper model must take. In particular, the nature of the flow field and the details of the chemical kinetics involved have not yet been established for even the simplest propellant systems. In view of these inadequacies in basic information, it is worthwhile to first examine a somewhat simplified model of the burning process, and to ascertain the general behavior of the model in relation to experimental findings. By this means, an indication of the validity of the approach should be obtained.

Accordingly, the immediate objective is more limited than the final goal. For the present, attention is confined to a laminar-flow, steady-state model with simplified reaction kinetics. However, the analysis is formulated so that subsequent inclusion of time variable phenomena and more sophisticated chemistry will present no essential difficulty, other than increased complexity.

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In building this theory, it would be most desirable to draw on the existing literature, and to achieve the desired goal by extension or generalization of existing theory. To this end, some effort has been devoted to surveying the pertinent literature. A few brief comments on the general features of existing combustion theory follow.

Excluding phenomenological approaches, the theoretical literature on solid propellant combustion may be divided into two classes according to whether the propellant surface is assumed to be homogeneous or heterogeneous. Theory based on homogeneous propellants would apply strictly only to monopropellants and double-base propellants, or possible fine-grained composites at low chamber pressure, all of which tend to produce a gas phase resembling a premixed flame. Studies of the heterogeneous surface are directed toward coarse composites, although the presence of erosion may in fact cause sufficient mixing that relatively coarse composites produce nearly premixed gases in the burning process. All non-steady analyses of solid propellant combustion have been based on the homogeneous propellant concept.

Most of the literature using the notion of premixed gases at the propellant surface has utilized somewhat artificial subdivision of the gas phase into distinct zones. Thus, there have been defined the foam zone, the fizz zone, the preparation zone, the flame zone, and more recently, the induction zone, the thermal layer, and so on. Related to this zone concept also is the postulate that heat transfer to the propellant can be described by a convective heat transfer coefficient. These concepts have proved useful in simplifying the analysis, and some success has been achieved in using them to predict over-all behavior. They do not, however, lend themselves to

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prediction of time-dependent behavior, or to fluid dynamic analysis simply because discontinuities are introduced at the zone boundaries.

Analyses have been made in which continuous behavior of the gas phase is postulated. These are essentially laminar flame analyses, and they bear a close relationship to the model under development.

Strictly theoretical predictions concerning the effects of erosion on the solid propellant burning seem to be non-existent. The closest approaches to a theory for this phenomenon are based on rather tenuous assumptions concerning the character of turbulent transport at the propellant surface. The recent acoustic studies of Hart, Bird, and McClure do not actually represent theories of erosion but rather are analyses of the consequences of a given kind of response of the propellant to unsteady erosion.

Examples of analyses using the concept of a heterogeneous surface are the original diffusion-flame model of Summerfield and his later granular diffusion flame approach, the two-temperature theory of Schultz and Dekker, and the sandwich propellant model studied by Nachbar.

Because of the obvious difficulty of three-dimensional effects arising from heterogeneity of the propellant surface, the homogeneous problem is being attacked first. Furthermore, the analysis is based on laminar flow since it is felt that the thin region wherein the major chemical reactions occur will fall in a laminar flow region, even though turbulent flow occurs elsewhere in the system. Basically, the over-all problem is analysis of a laminar flow of reacting gas over a chemically reacting surface.

The general features of the fluid dynamic model are shown in Figures 1a and 1b. Two-dimensional flow of combustion products over a plane propellant surface is postulated, and typical temperature and velocity

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profiles near the propellant surface are as shown in Figure 1b. In keeping with usual boundary layer concepts, thermal and momentum boundary-layer thicknesses can be defined on the basis of these profiles, as indicated in both figures. Concentration (or diffusion) boundary layer thicknesses may be defined in the same way. The fundamental equations which describe the velocity, temperature, and concentration fields in the gas phase then are the well-known boundary-layer forms of the conservation relationships; that is,

Continuity:

$$\frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} = 0 \quad (1)$$

$$\rho u \frac{\partial \alpha_i}{\partial x} + \rho v \frac{\partial \alpha_i}{\partial y} = \frac{\partial}{\partial y} \left(\frac{Le}{c_p} k \frac{\partial \alpha_i}{\partial y} \right) + w_i \quad (2)$$

Momentum:

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = - \frac{\partial p}{\partial x} + \frac{\partial}{\partial y} (\mu \frac{\partial u}{\partial y}) \quad (3)$$

Energy:

$$\rho \left(u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{k}{c_p} \frac{\partial h}{\partial y} - \frac{k}{c_p} \{Le - 1\} \sum_i h_i \frac{\partial \alpha_i}{\partial y} \right) \quad (4)$$

where

ρ is density

α_i is concentration of i^{th} component

Le is Lewis number

k is thermal conductivity

c_p is constant pressure heat capacity of the mixture

w_i is rate of production of i^{th} component by chemical reaction

p is pressure

μ is viscosity

h_i is enthalpy of i^{th} component

h is enthalpy of mixture $(\sum_i \alpha_i h_i)$

A further energy relation for the solid is required, and this is the usual heat conduction equation.

$$r \frac{\partial T}{\partial y} + \alpha_s \frac{\partial^2 T}{\partial y^2} = 0 \quad (5)$$

Here, α_s is thermal diffusivity of the solid and r is the rate of recession of the burning surface. It is presumed here that the zone of phase change and chemical reaction in the solid is very thin and may be regarded as a surface heat sink insofar as the heat conduction in the solid is concerned. Accordingly, conditions at the solid-gas interface are described by the following heat balance.

$$\left[k \left(\frac{\partial T}{\partial y} \right)_s = \left(k \frac{\partial T}{\partial y} \right)_g - \rho_s r Q_p \right]_{y=0} \quad (6)$$

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where subscripts s and g refer to the solid and gas, respectively, and Q_p is the heat absorbed in gasification of the solid.

Without the use of drastic simplifying assumptions, the complexity of this system of equations precludes analytical solutions. It is not intended to restrict the investigation to the domain of entirely analytical solutions, however. Numerical solutions utilizing high-speed computer techniques will be undertaken as required.

Examination of the conservation relations shows that the burning rate of the solid is directly related to the energy transfer across the gas-solid interface if no mechanical attrition is occurring. This energy transfer from gas to solid depends, to a small extent, on radiation, but mainly on temperature and concentration gradients in the gas at the surface and on the transport properties. Since temperature profiles in the gas phase, according to the energy relationships, depend on velocity distribution and chemical reaction rate, it is expected that the burning rate will be sensitive to both velocity distribution and chemical kinetics in the vicinity of the surface. Moreover, pressure gradients influence the velocity distribution of the boundary layer, and thereby the temperature profile and local chemical reaction rates. Thus, there should be interplay between pressure sensitivity and erosion sensitivity. In view of all of these observations, it would be surprising if the simple "erosion constant" concept were truly valid for real propellants.

According to present thinking, the model contains the following features:

1. Solid reaction is limited to pyrolysis at or very near the surface according to an Arrhenius law. This is an extreme simplification for the pyrolysis but it may at some future time be altered to conform with new information.

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2. Thermal properties of the solid are constant throughout.
3. Radiative energy transfer is negligible compared to heat conduction.
4. Transport properties of the gas phase may be represented by polyatomic relations based on kinetic theory.
5. Boundary-layer approximations hold for the gas phase.
6. Viscous energy dissipation is negligible.
7. Flow outside the boundary layer is isentropic.
8. The perfect gas law is obeyed.
9. A single-step unidirectional chemical reaction of second order occurs in the gas phase.

The last assumption is probably the most restrictive, and is adopted at this time for investigation of the general behavior of the theoretical model. Some justification for the use of second-order kinetics is to be found in the limited success of both Summerfield and Rosen in using such a model for predicting pressure dependence of the burning of ammonium perchlorate propellants at relatively low pressure.

In spite of the shortcomings of the proposed model, its solution for realistic values of the parameters involved will provide insight into some of the fundamental features of the burning process. Among these will be the effect of parallel gas flow (erosion) on the burning rate, as well as on the pressure dependence of burning rate. Furthermore, the distribution of chemical reactions in the gas phase may indicate regions which may, for the steady state, be treated by the concept of distinct zones, thus leading to some simplification of the steady-state problem.

It is recognized that the initial model is lacking in the details of the chemical kinetics. It is to be hoped, however, that some effort will be directed toward this area and new kinetic information for both the solid and

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gaseous phases will be forthcoming. In the meantime, there is hope of improving this model in respect to gas phase kinetics using present knowledge.

There exists no completely theoretical approach to the chemical kinetics problem; neither is direct experimental information available. However, there is an extensive literature on rather specific kinetic experiments. A large number of investigations have been performed on the lower molecular-weight hydrocarbons, both saturated and unsaturated. These investigations have led to fairly reliable values for activation energy and frequency factor in the Arrhenius expression for rate constant.

In view of the large literature on kinetics of lower hydrocarbons, it is possible that the collective results can be applied to the present problem. While the propellant fuel may exist in the solid state as a polymer of very high molecular weight, the solid surface achieves relatively high temperatures previous to vaporization, and the large molecular weight molecules are not stable at these temperatures. The polymer decomposition is probably a zero or first order reaction, which occurs at a rate several times faster than bimolecular reactions. It is believed that the over-all reaction may be a rather fast dissociation of the polymer into low molecular weight hydrocarbons, with subsequent gas phase oxidation. In that case, the existing literature may be used for the determination of the reaction rate constants for a postulated reaction mechanism. Using a chemical model based on kinetic information of this sort, improvement of the combustion model will be attempted. It may also be found whether the single-step chemical reaction now being investigated yields results comparable to those for the more elaborate chemical model.

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Finally, extension of the analysis to the unsteady state will be undertaken using as few restrictive assumptions as possible. Here, also, we will wish to investigate whether simplified chemical models can be used to represent the actual combustion chemistry. Our final goal, to reiterate, is a valid model for unsteady combustion and erosion of solid propellants. The importance of such a model to understanding of the combustion instability phenomena cannot be overstated.

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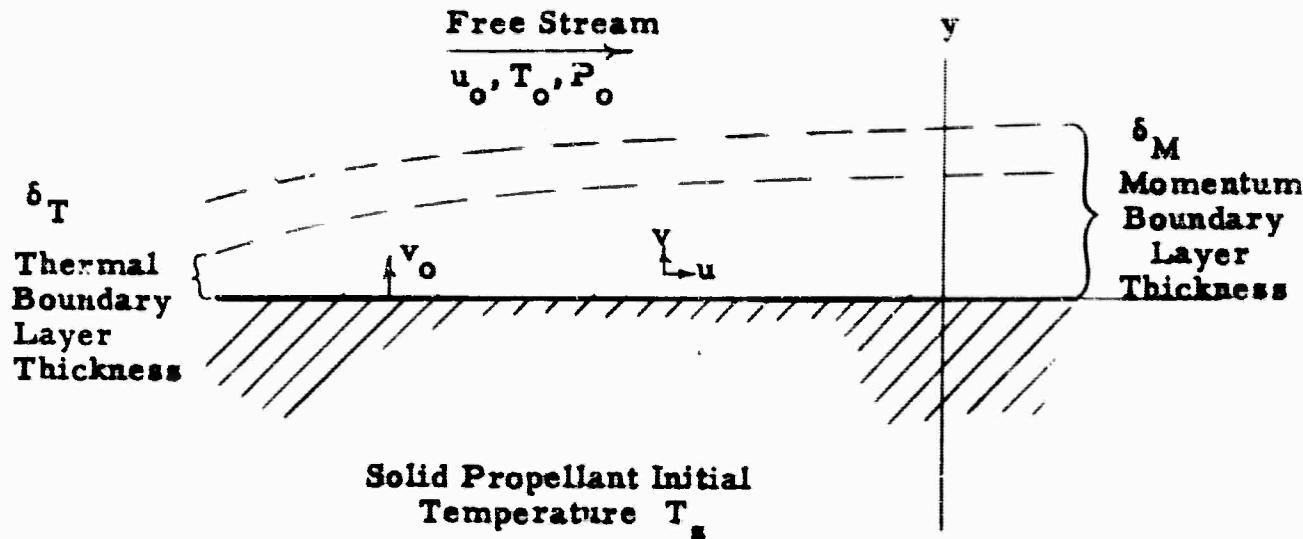


Figure 1a - SCHEMATIC REPRESENTATION OF THE BOUNDARY LAYER MODEL

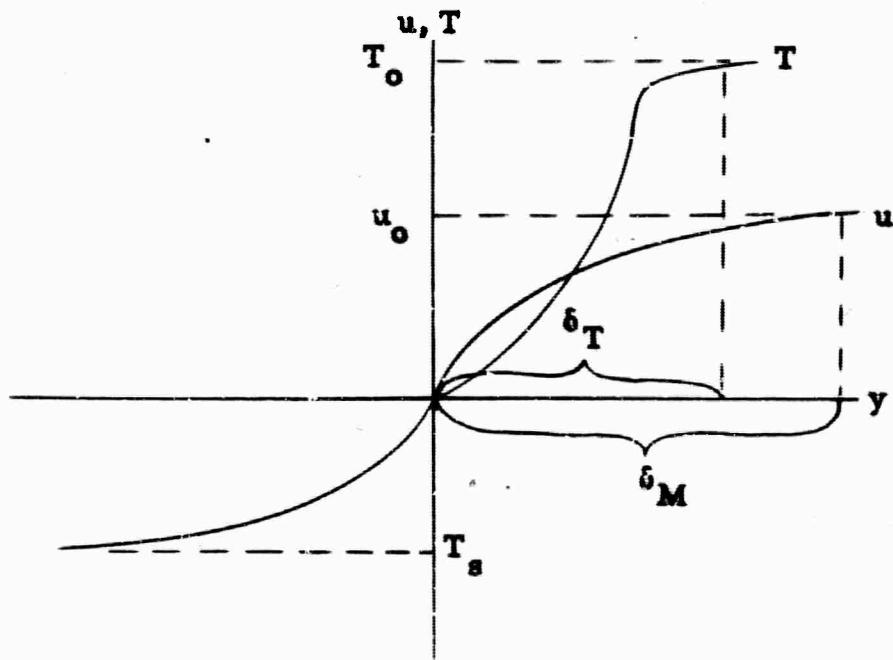


Figure 1b - TYPICAL PROFILES OF TEMPERATURE AND VELOCITY